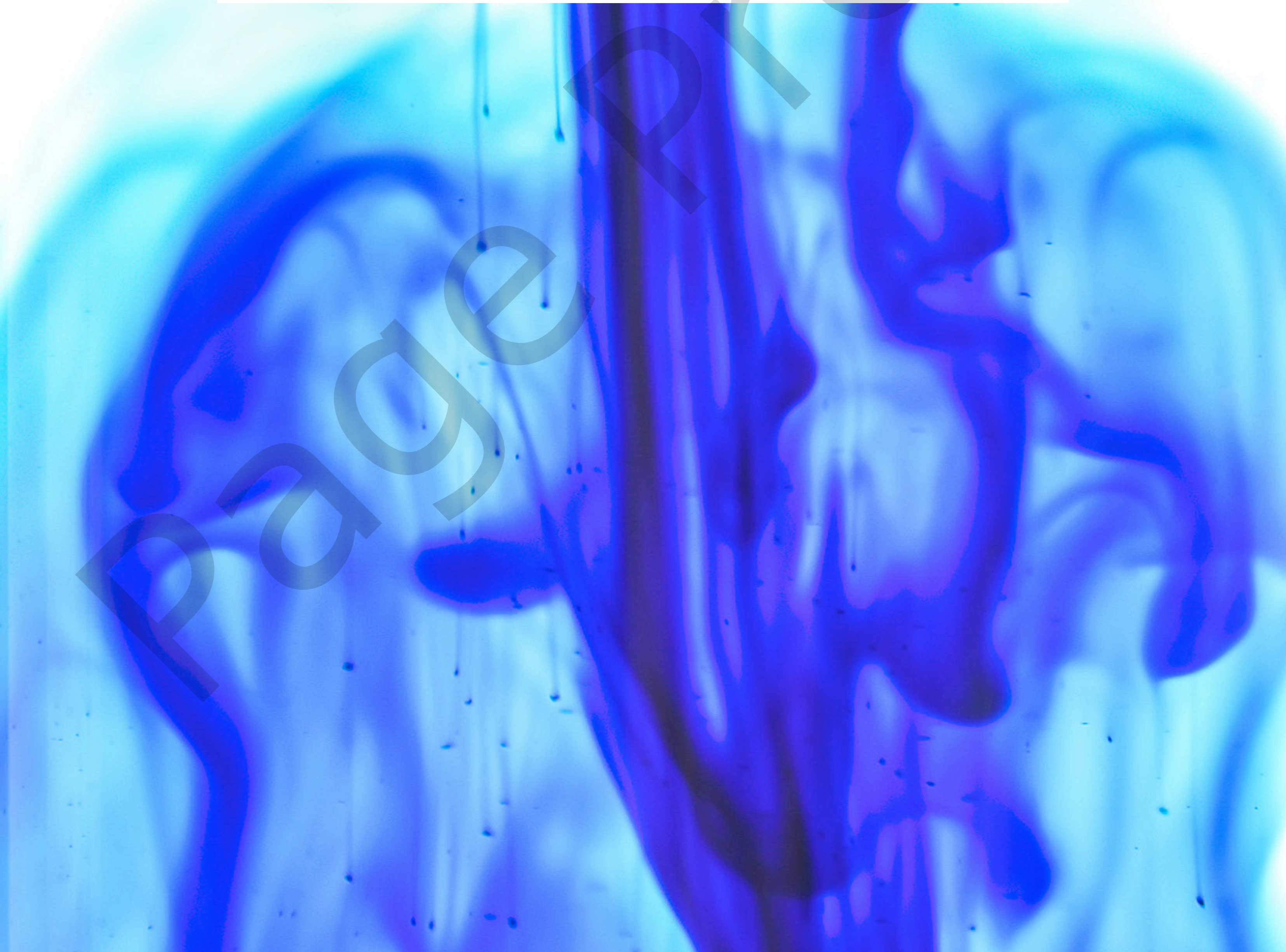
CHAPTER

06 Indicators

In this chapter, you will apply your understanding of acid–base equilibrium systems to indicators. Indicators are used to distinguish between acids and bases and to determine the pH of a solution. Indicators exist in two forms: a weak acid and its conjugate base. These two forms of the indicator are different colours. When an indicator is added to a solution, the pH of the solution will determine whether the indicator exists mostly in its acidic or basic form and hence the colour of the solution.

Science understanding

- acid–base indicators are weak acids, or weak bases, in which the acidic form is a different colour from the basic form



6.1 Characteristics of indicators

One of the characteristic properties of acids and bases is their ability to change the colour of certain plant extracts. Litmus is a purple dye obtained from lichen. In the presence of acids, litmus turns red. The colour of rose petals, blackberries and red cabbage is also altered by acids and bases. Such plant extracts are called **indicators**. Common indicators and their pH ranges can be seen in Figure 6.1.1. Today, most indicators used in laboratories and industry, such as bromothymol blue, methyl orange and phenolphthalein, are synthetic.

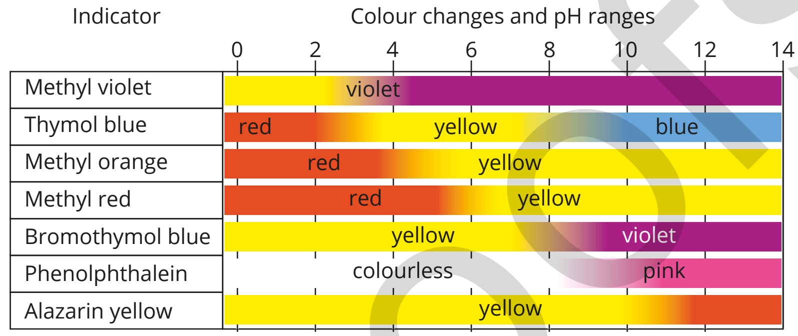


FIGURE 6.1.1 Common indicators and their pH ranges

Indicators are weak acids or weak bases. The conjugate acid form of the indicator is one colour and the conjugate base form is another. Indicators that undergo a single colour change are used for many analyses.

Figure 6.1.2 shows the variation in colour that can be achieved when red cabbage is used as an indicator. The colour of juice extracted from the leaves of red cabbage depends on the pH of the solution.

FIGURE 6.1.2 The colour of extract from red cabbage in solutions (from left, clockwise) of pH 1, pH 3, pH 5, pH 8 and pH 10

PROPERTIES OF INDICATORS

Indicators are large organic molecules whose colour changes in response to changes in the pH of the solution they are dissolved in. They are either weak acids or weak bases.

In solution, the acidic form of the indicator is in equilibrium with its conjugate base as shown in the following equation:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

The position of equilibrium depends on the pH.

The acidic form of an indicator (HIn) and the conjugate base form (In^-) are different colours. The colour of the acidic or basic form is visible at low indicator concentrations. Changing the pH of an indicator solution changes the relative concentrations of the acidic and basic forms and hence the overall colour of the solution can change.

The characteristics of some common laboratory indicators and how their colour changes with pH will be discussed in the following section.

Remember from Chapter 4 that, according to the Brønsted–Lowry definition of acids and bases, acids and their conjugate base differ by the presence of a proton (H^+).

CHEMFILE

Plant colour and pH

Irish chemist Robert Boyle (1627–91) is credited with conducting the first systematic investigation into the colour of plant extracts in acidic and basic solutions. As part of his investigations, he soaked paper in litmus extract. Litmus is a dye obtained from lichens. In the presence of acids, litmus turns red (Figure 6.1.3), and in the presence of bases, it turns blue.

Boyle used the dried litmus paper to identify substances as either acids or bases. Litmus paper is still used for this purpose today.

FIGURE 6.1.3 Blue litmus turns red in the presence of citric acid, a component of lemon juice.

6.1 Review

SUMMARY

- Indicators are large organic molecules that change colour in solution at different pH values.
- Indicators are either weak acids or weak bases.
- In solution, the acidic form of an indicator is in equilibrium with its conjugate base.
- Depending on the pH of the solution, the position of the equilibrium between the acidic and basic forms of an indicator changes.
- The colour of the acidic form of an indicator is different from the colour of its conjugate base.

KEY QUESTIONS

1 A substance has the following properties. Which one or more of these properties would make this compound unsuitable for use as an indicator?

A The compound is a weak acid.

B The compound turns dark blue in acidic solutions but is colourless in basic solutions.

C The compound colours are only visible at high concentrations of the compound.

2 Referring to Figure 6.1.1 on page 138, at what pH range would you expect:

a methyl violet to appear yellow?

b phenolphthalein to appear pink?

c methyl red to change colour from red to yellow?

6.2 Common indicators

Indicators are used to provide information about the pH (and therefore acidity and properties) of a chemical. As seen in Figure 6.1.1 on page 138, a number of indicators are commonly used in laboratories. Each indicator has a unique pH range in which they change colour. Indicators are different colours in acidic solutions and basic solutions. Commonly used indicators, their colours and the pH ranges in which they change colour will be discussed in this section.

UNIVERSAL INDICATOR

Universal indicator (Figure 6.2.1) is widely used to estimate the pH of a solution. It is a mixture of several indicators and changes through a range of colours, from red through yellow, green and blue, to violet. If a more accurate measurement of pH is needed, you can use a pH meter instead of universal indicator.

FIGURE 6.2.1 Universal indicator pH scale. When universal indicator is added to a solution, it changes colour depending on the solution's pH. The tubes contain solutions of pH 0 to 14 from left to right. The green tube (centre) is neutral, pH 7.

BROMOTHYMOL BLUE

Bromothymol blue is a widely used indicator. The indicator is yellow in acidic solutions and blue in basic solutions. In a neutral solution of pH 7, the indicator is green, midway between yellow and blue.

A chart showing the variation in colour of bromothymol blue from pH 0 to pH 14 is shown in Figure 6.2.2. Bromothymol blue changes colour between pH 6.0 and pH 7.6.

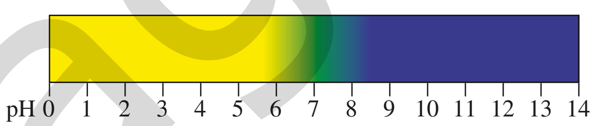


FIGURE 6.2.2 Bromothymol blue is yellow in acidic solutions and blue in basic solutions.

The equilibrium principles studied in Chapter 2 apply to indicators. You can use Le Châtelier's principle to predict the colour of an indicator, such as bromothymol blue, in acidic and basic solutions.

Bromothymol blue is a complex organic compound. The equation for the ionisation of bromothymol blue in water is shown here. For the sake of simplicity, the acidic form of bromothymol blue can be represented as HBB and the basic form as BB^-.

$$\underset{\text{yellow}}{HBB(aq)} + H_2O(l) \rightleftharpoons \underset{\text{blue}}{BB^-(aq)} + H_3O^+(aq)$$

The indicator colour you see depends upon the relative concentrations of HBB and BB^-.

When a few drops of bromothymol blue indicator are added to HCl solution, the additional H_3O^+ ions from HCl cause the indicator equilibrium system to shift to the left to oppose the increase in the concentration of the H_3O^+ ions.

$$HBB(aq) + H_2O(l) \rightleftharpoons BB^-(aq) + H_3O^+(aq)$$
$$\Longleftarrow$$

The concentration of HBB molecules becomes much greater than the concentration of BB^- ions and the solution has a yellow colour.

When the indicator is added to a solution of a base, the system to shifts to the right to oppose the increase in the concentration of the OH^- ions.

$$HBB(aq) + H_2O(l) \rightleftharpoons BB^-(aq) + H_3O^+(aq)$$
$$\Longrightarrow$$

This (forward) reaction can also be written as shown below with the OH^- ions reacting with the HBB:

$$HBB(aq) + OH^-(aq) \rightleftharpoons BB^-(aq) + H_2O(l)$$

The concentration of BB^- ions becomes much greater than the concentration of HBB molecules and the solution is blue in colour (Figure 6.2.3).

At pH 7, the concentrations of HBB molecules and BB^- ions are equal. This is referred to as the **transition point** of bromothymol blue. At this point, the solution appears green, a mixture of blue and yellow. The transition point is the midpoint of the indicator colour change.

FIGURE 6.2.3 Bromothymol blue is yellow in acidic solutions (left), blue in basic solutions (right) and green in neutral solutions (centre).

Le Châtelier's principle states that if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of the change. The addition of a strong base to a solution reduces the concentration of H_3O^+ ions. For indicator solutions, this causes a shift in the position of the equilibrium between its acid and conjugate base forms, forming more of the base form of the indicator.

METHYL ORANGE

Methyl orange is a synthetic indicator often used in the analysis of weak bases. It is also used as a textile dye.

Methyl orange is red in acidic solutions and yellow in basic solutions. The indicator changes colour between pH 3.1 and pH 4.4. Between these pH values, the indicator is orange. A colour chart for methyl orange indicator is shown in Figure 6.2.4.

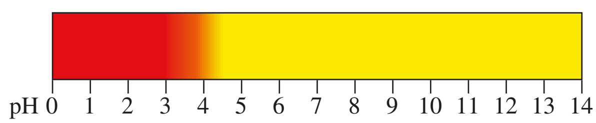
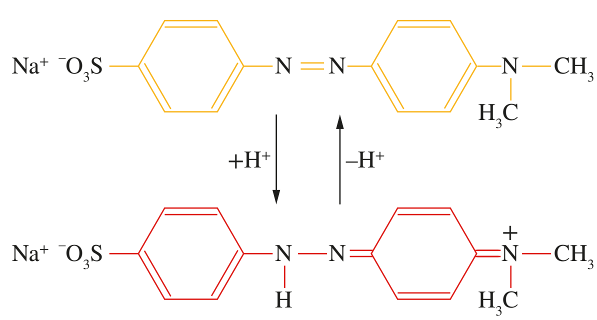


FIGURE 6.2.4 Methyl orange is red in acidic solutions and yellow in basic solutions. The indicator changes colour over the pH range 3.1 to 4.4.

Methyl orange is a weak acid. The acidic and basic forms of the indicator are in equilibrium in solution. Their structures are shown in Figure 6.2.5.

yellow form of methyl orange at pH values greater than about 4.5



red form of methyl orange at pH values less than about 3

FIGURE 6.2.5 The structure of methyl orange is dependent upon the pH of the solution. The red form of methyl orange has a different structure from the yellow form.

PHENOLPHTHALEIN

Phenolphthalein is a synthetic indicator used in the analysis of weak acids. It has also been used as the active ingredient in some laxatives. In acidic solutions, phenolphthalein is colourless, whereas in basic solutions it has a pink colour. Phenolphthalein changes colour over the pH range 8.3–10.0.

A colour chart for phenolphthalein indicator is shown in Figure 6.2.6.

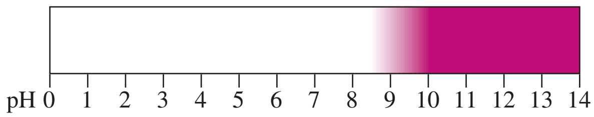


FIGURE 6.2.6 Phenolphthalein is colourless in solutions when the pH is below 8.3 and pink when the pH is greater than 10. The indicator changes colour over the pH range 8.3 to 10.0.

CHEMISTRY IN ACTION

Phenolphthalein and the carbonation of concrete

Phenolphthalein is used to determine the extent of carbonation in concrete—the reaction of concrete with atmospheric carbon dioxide.

As concrete sets, atmospheric carbon dioxide reacts with water, forming carbonic acid:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

The carbonic acid reacts with lime ($Ca(OH)_2$) in the concrete to form calcium carbonate. Calcium carbonate binds to the silicates in the sand, increasing the strength of the concrete:

$$H_2CO_3(aq) + Ca^{2+}(aq) + 2OH^-(aq) \rightarrow CaCO_3(s) + 2H_2O(l)$$

Hydroxide ions are consumed in this reaction, lowering the pH. Steel rods used to reinforce concrete begin to corrode when the pH is below 8. Corrosion of these rods weakens the concrete structure.

The extent of carbonation is determined by spraying a concrete section with phenolphthalein. As shown in Figure 6.2.7, the area unaffected by carbonation, which has a high pH, shows up as pink. The indicator will remain colourless in the carbonated area because the pH is below 8.3.

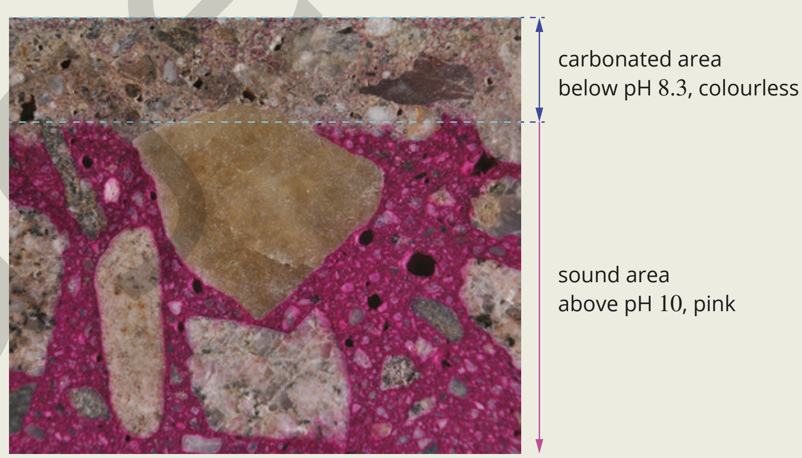


FIGURE 6.2.7 Phenolphthalein is used to indicate the extent of carbonation in concrete. The clear section has been affected by carbonation while the pink section is unaffected.

6.2 Review

SUMMARY

- An equilibrium exists between the acidic and basic forms of an indicator. The equilibrium can be represented by the equation:

  $HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$
- The colour change of an indicator can be explained by the equilibrium shifts that occur when H_3O^+ ions or OH^- ions are added.
- Under acidic conditions, the equilibrium is shifted to the left, resulting in a higher [HIn]. As a result, the solution has the colour of the acidic form of the indicator.
- Under basic conditions, the equilibrium is shifted to the right, producing more In^- ions. As a result, the solution has the colour of the basic form of the indicator.
- Indicators appear different colours when in the acidic form compared to when in a basic form.
- A variety of indicators are available and each changes colour over a unique pH range. Table 6.2.1 provides a summary of the indicators discussed in this chapter.

TABLE 6.2.1 Colour of indicators in acid and basic forms

Indicator	Colour in acidic form	Colour in basic form
Universal indicator	Universal indicator is a mixture of several indicators and changes through a range of colours, from red through yellow (in acidic solutions), green (neutral solutions) and blue to violet (in alkaline solutions).	
Bromothymol blue	Yellow	Blue
Methyl orange	Red	Yellow
Phenolphthalein	Colourless	Pink

KEY QUESTIONS

1 Four beakers contain solutions of lemon juice, ammonia solution, sugar and sodium hydroxide. Some phenolphthalein is added to each beaker. In which beakers does the phenolphthalein change colour?

2 Methyl red is red in acidic solutions and yellow in basic solutions. It changes colour between pH 4.4 and pH 6.7. The acidic form of the indicator can be represented as HIn and the basic form of the indicator can be represented as In^-.

a Complete the equation below by filling in the gaps.

$\_\_\_\_ + H_2O(l) \rightleftharpoons \_\_\_\_ + H_3O^+(aq)$

b A few drops of methyl red are added to a solution that has a pH of 3. What would you expect to happen to the reaction equilibrium?

3 A solution is yellow with both bromothymol blue and methyl orange. Which one of the following is the most accurate approximation of the pH of this solution?

A Between 3.1 and 6.0

B Between 4.4 and 6.0

C Between 3.1 and 7.6

D Between 4.4 and 7.6

4 Four beakers each contain a solution with a pH of 9. What is the colour of each solution after the addition of:

a universal indicator?

b bromothymol blue?

c methyl orange?

6.3 pH range of an indicator

As you have seen earlier in this chapter, indicators do not necessarily change colour at pH 7. Bromothymol blue changes colour between pH 6.0 and pH 7.6. Methyl orange changes colour between pH 3.1 and pH 4.4. Phenolphthalein changes colour over a pH range of 8.3–10.0. The range of pH values over which an indicator changes colour is known as the **indicator range**.

The acid and base colours and pH ranges of some common laboratory indicators were shown in Figure 6.1.1 on page 138.

Table 6.3.1 summarises common indicators and their pH ranges.

TABLE 6.3.1 Common indicators and their pH ranges

Indicator	Colour in acidic solution	Colour in basic solution	pH range
Methyl violet	Yellow	Violet	0.0–1.6
Methyl orange	Red	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.4–6.2
Bromothymol blue	Yellow	Blue	6.0–7.6
Phenolphthalein	Colourless	Pink	8.3–10.0
Alizarin yellow	Yellow	Red	10.0–12.0

A neutralisation reaction occurs when an acid reacts with a base to form a salt and water.

USING INDICATORS

The reactions of acids were discussed in Chapter 4. Indicators are particularly useful in determining the equivalence point of a neutralisation reaction between an acid and a base. The **equivalence point** is the point during a neutralisation reaction when the amount of acid and base are in the stoichiometric ratio represented by the reaction equation.

For example, hydrochloric acid and sodium hydroxide react according to the following equation:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

The equivalence point during this reaction is when the amounts (in mol) of HCl and NaOH are equal in the 1:1 ratio given by the equation.

Indicators are commonly used in volumetric analysis or titrations to help visualise the equivalence point of a reaction. **Volumetric analysis** is a quantitative technique in which volumes of solutions of known concentrations are added to volumes of solutions of unknown concentrations. A **titration** is a form of analysis in which a base of known concentration and volume is reacted with an acid of unknown concentration. The volume needed to neutralise the base can be used to determine the concentration of the acid by stoichiometric calculations. The concentration of a base can also be determined by titration with an acid of known concentration and volume.

In titrations, accurate glassware such as burettes, volumetric flasks and pipettes are used to measure the volumes so you can accurately determine the amount (in moles) and concentration of solutions involved in the reaction. Volumetric analysis will be discussed in more detail in Chapter 7.

The **end point** of the indicator is the point in a titration when the indicator changes colour. It is vital that an indicator is chosen that changes colour sharply in the region of the equivalence point. At this point, the colour of the indicator will be intermediate between its colour in acidic solution and its colour in alkaline solution.

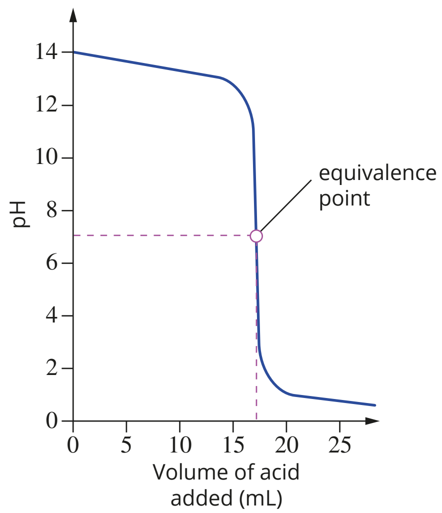


FIGURE 6.3.1 Titration curve for a strong acid being added to a strong base

When a strong acid such as HCl is titrated against a strong base such as NaOH, the change in pH can be graphed to produce a **titration curve** or **pH curve**. The equivalence point occurs when the gradient of the pH curve is steepest. An example of a pH curve is shown in Figure 6.3.1.

Near the equivalence point, the addition of a very small volume of HCl produces a large change in pH. In this titration, the pH changes from 10 to 4 with just one drop of acid. By using an indicator that changes colour in this pH range (for example, bromothymol blue pH range 6.0–7.6), one drop will cause a colour change. This is referred to as a sharp end point. Therefore, it is important to know the pH range of an indicator to ensure a sharp end point. Other indicators, including phenolphthalein (pH range 8.3–10.0), could also be used for this titration because they would also produce a sharp end point.

EXTENSION

Determining transition point and pH range of an indicator

Remember that indicators are weak Brønsted–Lowry acids. The acid–base equilibrium can be represented by the general equation:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

HIn represents the acidic form of the indicator and In^- represents the basic form.

The expression for the acidity constant for this general reaction is:

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]}$$

The pH at which the indicator changes colour depends upon the value of the indicator's acidity constant, K_a. At the midpoint of the indicator colour change, the transition point, the concentrations of the acidic and basic forms of the indicator are equal, i.e. $[HIn] = [In^-]$.

At the transition point, the equilibrium expression simplifies to $[H_3O^+] = K_a$.

The pH at the transition point can be calculated using $pH = -\log_{10}[H_3O^+]$. As a rule of thumb, the indicator range is one pH unit either side of the pH at the transition point.

Figure 6.3.2 shows the colour of phenol red at different pH values. Phenol red has a K_a of 10^{-8}. The concentration of hydronium ions at the transition point is therefore 10^{-8} mol L^{-1} and the pH is 8. The pH range of this indicator is approximately 8 ± 1, i.e. between pH 7 and pH 9.

FIGURE 6.3.2 Phenol red indicator at pH 5, pH 8 and pH 11.

6.3 Review

SUMMARY

- The point during a titration at which the reactants are present in equivalent amounts, as indicated by the coefficients in the equation for the reaction, is called the equivalence point.
- The end point is the point during the titration at which the indictor changes colour.
- Indicators used in titrations should be chosen so that they give a sharp end point.
- The end point in an acid–base titration must be at or close to the equivalence point.

KEY QUESTIONS

1 Explain the difference between the end point and equivalence point of a titration.

2 The acidic form of alizarin yellow is yellow, whereas its basic form is red. At pH 11, the concentrations of the acidic form and its conjugate base are equal. Which one of the following statements about alizarin yellow is correct?

A Alizarn yellow changes colour at exactly 11.

B A solution of alizarin yellow at pH 11 is neutral.

C The indicator can be used to distinguish between a solution of pH 9 and a solution of pH 13.

3 Congo red is an acid–base indicator. The acid colour of the indicator is blue and the base colour is red. The acidic form of the Congo red molecule can be written as HCgr.
At pH 4 (the transition point), the concentration of HCgr is the same as the concentration of its conjugate base, Cgr^-.

a Complete the balanced equation that represents the ionisation of Congo red in aqueous solution.
$HCgr(aq) + H_2O(l) \rightleftharpoons$ _____ + _________

b What will the colour of the solution be:

i at pH 4?

ii in a neutral solution?

iii at pH 2?

iv at pH 12?

Chapter review

06

KEY TERMS

bromothymol blue
end point
equivalence point
indicator
indicator range
methyl orange
pH curve
phenolphthalein
titration
titration curve
transition point
universal indicator
volumetric analysis

Characteristics of indicators

1 Write the general equation for the equilibrium that exists between the acidic form of an indicator and its conjugate base.

2 Which of the following statements about acid–base indicators is not true?

- **A** Indicators are coloured compounds that change colour as the pH of a solution changes.
- **B** Indicators can act as weak acids.
- **C** All indicators are derived from plant extracts.
- **D** Indicator colours are visible at low concentrations of the indicator.

Common indicators

3 Refer to Figure 6.1.1 on page 138 to determine what colour the following indicators will produce in pure water.

- **a** Methyl orange
- **b** Phenolphthalein
- **c** Bromothymol blue

4 State whether the following indicators are natural or synthetic in origin. If natural, what have they been extracted from?

- **a** Methyl orange
- **b** Litmus
- **c** Bromothymol blue

5 Why does universal indicator appear coloured across a range of pH values?

6 Bromothymol blue is added to a solution of pH 5.

- **a** What colour would the solution be?
- **b** What does this indicate about the position of the equilibrium of the indicator reaction?

pH range of an indicator

7 At what pH would phenolphthalein provide a sharp end point during a titration and what colour would you expect to see at the end point of the titration?

8 Define 'end point' and 'equivalence point'.

Connecting the main ideas

9 Why is it important to select an indicator with an end point close to the equivalence point for the reaction?

10 Use Le Châtelier's principle to explain why indicators are different colours in acidic and basic solutions.